

EXPERIMENT 1
MELTING POINTS

A. PRELAB ASSIGNMENT

1. Prepare a Table of Physical Constants in your notebook listing, in order, structure, formulae, and melting point ranges of the following substances:
 - a. Benzoic acid
 - b. Biphenyl
 - c. 4-Bromobenzophenone
 - d. 2,4-Dichlorobenzaldehyde
 - e. (d,l)- α -Hydroxy-phenylacetic acid [(d,l)-mandelic acid]
(Be sure to look up **(d,l)**, not just **d** or just **l**.)
 - f. Propanedioic acid (malonic acid)
 - g. Urea
 - h. Vanillin (also called Vanillin)

This table should follow the experiment title on the first (left-hand) page of the experiment.

Prepare tables to record melting points in the Data/Observation section, as follows:

Substance	Melting Point Range ($^{\circ}$ C)
A	
B	
A + B	
UNKNOWN	

POSSIBILITY 1 (P1)	
POSSIBILITY 2 (P2)	
UNKNOWN	
UNKNOWN + P 1	
UNKNOWN + P 2	

B. THEORETICAL BACKGROUND

Theoretical Definition of Melting Point

The melting point of a solid is the temperature at which the solid and its liquid form are in equilibrium, i.e., molecules move back and forth between the two states at the same rate, so both phases remain present. If the temperature of a solid is measured carefully as the solid is heated, the temperature will be observed to rise until the melting point (m.p.) of the solid is reached, and then the temperature will remain almost constant while the solid melts. The heat absorbed during melting is the “heat of fusion,” the energy needed to move the molecules out of the crystal lattice of the solid. When the solid has completely melted, the addition of more heat again contributes to an increase in the temperature of the sample, now a liquid. This describes the melting of a pure solid. The melting point is characteristic of the compound, independent of source, purification procedure, etc., and is useful in identifying the compound. However, many different compounds have identical or very similar melting points.

Functional Definition of Melting Point

Strictly speaking, the melting point is never a “point”. It is invariably a narrow range, about 1° for most compounds, but 0.5° for some, 1.5 – 2.0° for others. Part of the range is an experimental artifact. Since heat transfer is often uneven, all parts of a solid sample are unlikely to be at the same temperature simultaneously. While some regions of the sample may be at the melting point (solid and liquid in equilibrium), other regions may be at slightly higher or lower temperatures. Thus, visible melting will occur over a range of temperatures. Therefore, the proper report of a melting point is the temperature range from the first visible appearance of liquid (distinguished from “softening” of the crystal) to the disappearance of the last visible crystal of solid. The end is the most important point, but the whole range is needed for full interpretation (e.g. benzoic acid, m.p. = 120 – 121.5°C).

Melting points for many organic compounds may be found in the CRC Handbook of Chemistry and Physics. These “literature” melting points are taken from reports in the chemical literature and indicate the melting range or upper end of the melting range of very pure samples of compounds. Consequently, these values are the highest values that can be expected for each compound. (See below for effects of impurities on melting points.) In some cases, more than one melting point will be listed for a single compound. This usually means that the compound can exist in more than one type of crystal lattice and that the different types have different stabilities and thus will break down at different temperatures.

Effects of an “Impurity”

If two different compounds, A and B, are intimately mixed, the melting point behavior of the mixture differs from that of either pure compound. When a small portion of B is mixed with A, the upper limit of the melting point range of A is lowered. Increasing the amount of B in A continuously decreases the upper limit of the melting range of the resultant mixture until such point that B ceases to be the impurity in A, and A then becomes the impurity in B. The point at which this occurs is called the eutectic; the eutectic temperature and composition of a mixture varies with the nature of the components A and B.

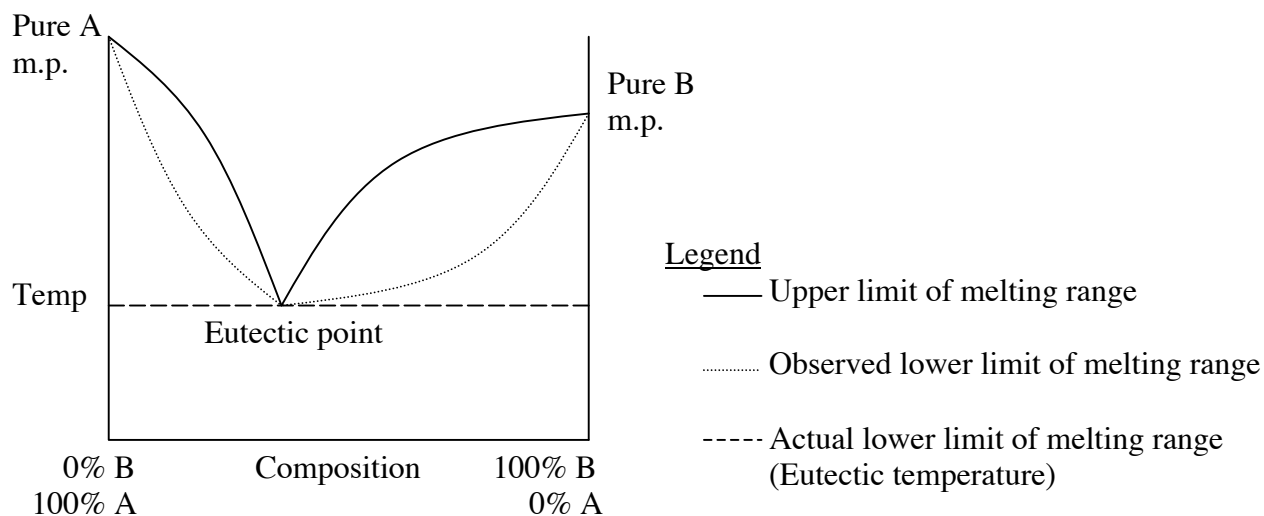


Figure 1. Melting Curves of Mixtures of A and B

The melting point of a eutectic mixture is below that of either pure A or pure B and is the lowest temperature at which any mixture of A and B can melt. The lower limit of the melting range of all mixtures of A and B is actually equal to the eutectic temperature because that part of the mixtures which is of the eutectic composition melts at the eutectic temperature. Actual observation of the true lower limit is difficult in all mixtures and impossible in mixtures containing little of one component. In most mixtures, the small amount of material that consists of the eutectic composition, and therefore melts first, is obscured by the relatively large amount of remaining "pure" component. The upper limit of the melting range is more readily observed, since it is much easier to note the disappearance of the last crystal in the liquid than appearance of the first drop of liquid in the mass of solid. The upper limit of the melting range of a compound containing an impurity is always lower than that of the pure compound.

Mixed Melting Points

The melting point of a compound is a physical characteristic often used to identify the compound and provide information about its purity. Pure compounds melt sharply. The presence of an impurity in a sample lowers the upper end of the melting range and very often causes the observed melting range to be wider than that of the pure compound. Therefore, if two samples of similar melting point are intimately mixed, and the melting point of the mixture is not "depressed" or "broadened," the two samples are the same compound. If two samples are mixed, and the m.p. of the mixture is depressed and possibly broadened, the two samples cannot be the same compound. When attempting to identify a compound by the mixed melting point method, it is critical to observe the melting behavior of the unknown and standard side by side with the mixture. The procedure gives a direct comparison of the mixture with the standards and allows you to easily observe any variation of melting behavior between samples under your experimental conditions. It is also useful to test a second possibility to assure

that under the conditions of your experiment the technique is capable of distinguishing between different compounds.

General Procedures

a. Filling the Melting Point Tube

Points to remember: Use the spatula attached to each bottle to take small samples (the tip of the spatula) on labeled pieces of paper. To avoid contamination, never return excess samples to bottles; instead, share with a neighbor. Grind the samples several times with a spatula on weighing paper to form a fine powder. This will facilitate uniform heat transfer throughout the sample. If melting points are to be compared, they should be taken side by side when possible. Fill one m.p. tube for each sample or each mixture, and store all tubes in slits in labeled papers.

b. The Melting Point

The melting point in a capillary tube is taken as the temperature range between the appearance of the first droplet and the disappearance of the last crystal. A shrinking or sintering may be visible a few degrees below the m.p. The actual melting range should be determined slowly over a period of 30 sec. This can be achieved by adjusting the heating rate to 2°/min. (See Section C below, Use of Hoover M.P. Apparatus.) Even under carefully controlled conditions, slight variations in experimental m.p. can occur.

c. Use of the Hoover Melting Point Apparatus

The Hoover m.p. apparatus used in our laboratories contains a beaker filled with silicone oil, which is electrically heated and stirred. The melting point tube rests on a platform that is illuminated and viewed with a lens.

To use the apparatus:

1. Turn power switch on.
2. Insert your melting point tube into the holes in the top of the apparatus (there is room for 5 tubes).

Never leave the apparatus unattended with the heater on!

3. Turn stirrer to the highest setting that does not cause excessive bubbles.

4. Turn heater dial to a setting that will cause the rate of heating to be $2^{\circ}/\text{min}$. during the melting of the compound. This slow heating is important since, if the rate of temperature change is too rapid, the experimental m.p. will generally be too high. If the heating is too rapid, the temperature will usually change significantly between the time that the last crystal melts and the time that the temperature is read from the thermometer. The appropriate setting varies from one apparatus to another. Generally, a heater dial setting of anywhere from 3 to 4 will give the proper heating rate for compounds melting at 135°C , i.e., the actual melting point process will take 30 seconds to occur. If, after melting is complete, the temperature continues to rise spontaneously more than 5°C , the heating was too rapid, and the melting point is inaccurate and should be repeated using a lower setting on the heater dial.

In order to approximate the proper dial setting, one must have a rough idea of the melting point of the compound. If you know the identity of the compound, look up the expected melting point in your Table of Physical Constants. If the compound is an unknown or a mixture, do a rapid melting point determination to get the approximate melting point range, i.e., determine the melting point very roughly as being 120 or 140 degrees, etc. Then cool down the m.p. apparatus to about 20 degrees below the expected melting point, set the heater dial to give a heating rate of $2^{\circ}/\text{min}$ at the expected melting point, and determine the melting range of another sample precisely.

Important: The range from first liquid to the melting of the last crystal is the m.p., but only solid in contact with liquid is watched, not solid above the melt.

5. Record the melting ranges of samples and discard the used tubes.
6. Turn all dials back to zero and turn power switch off.

B. PROCEDURE FOR THE LAB PERIOD

Check in – Do this as time permits

Check each item in your drawer and cupboard against the Check List. Be sure all glassware is clean and unbroken. There is a labeled display of apparatus available in the laboratory. On a separate sheet of paper, make a list of missing items, so that the instructor can get them for you; include your name and desk number. Sign your check list and return it to the instructor.

Melting Points

1. Standard compounds and unknown compounds will be available on the reagent shelf.
2. To observe the effect of mixing two different compounds of similar m.p., prepare one capillary tube with pure A, one with A and B well mixed, and one with pure B.
3. Identification of your unknown.
Record the number of your unknown and then prepare a capillary for determining its melting point. The sample will be used to determine a rough melting point, so that you can choose the two best possibilities from the standards for further comparison.
4. Attach melting point tubes prepared in steps 2 and 3 to labeled slits in paper (in the order listed in your data table). Take the tubes to an available Hoover apparatus and insert the tubes in the order shown in your data table. To save time, heat the oil rapidly (setting of 4 or less) until thermometer reads 50°C, then turn the dial down to a setting of about 2 which should establish the 2°/min increase in temperature. Once this rate is attained, gradually increase the dial setting as necessary to maintain the 2°/min rate. As the samples melt, record the melting range of each sample directly in the table in your lab notebook.
5. Your unknown is one of the compounds listed in your prelab assignment. Devise a procedure to identify your unknown by mixed melting point method.. Describe this procedure in your notebook. Record all data in a table on the page opposite the procedure. One possible plan is to compare the melting

point of your unknown against those listed in your Table of Physical Constants. When comparing melting point values, experimental results should be obtained side by side when possible. At least two known compounds should be tried.

Report your Results in a tabular format.

(For this experiment, this may mean recopying your Data table.)

D. QUESTIONS

1. In one sentence, describe the effect on the melting point of mixing two different compounds of similar m.p.
2. Identify your unknown. Give the reasoning that lead to your conclusion. (Be brief.)
3. An unknown compound A (m.p. = 130 – 131°C) is mixed with another unknown compound B (m.p. = 130 – 131°C). The mixture of A and B melts at 127 – 130°C. What conclusion can be drawn from this experiment? Explain.

E. DISCUSSION AND CONCLUSION

Discuss your results for both parts of the experiment and draw the conclusions. Be brief.